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L12: Entry 6 of 25 File: USPT May 22, 2001

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DOCUMENT-IDENTIFIER: US 6235695 B1

TITLE: Cleaning agent with oligoammine activator complexes for peroxide compounds

DATE-ISSUED: May 22, 2001

INVENTOR-INFORMATION:

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PRIOR-ART-DISCLOSED:

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ART-UNIT: 171

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ABSTRACT:

Complexes of the transition metals cobalt, iron, copper, and ruthenium having at least one and preferably at least five ammonia ligands are used to activate peroxygen compounds in aqueous cleaning solutions for hard surfaces. Compositions preferably contain 0.0025% to 0.25 by weight of the activating complex.

16 Claims, 0 Drawing figures

L12: Entry 6 of 25 File: USPT May 22, 2001

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Nitsch; Christian	Duesseldorf			DE

US-CL-CURRENT: 510/220; 134/25.2, 252/186.26, 252/186.28, 252/186.33, 510/221, 510/224, 510/372, 510/376, 510/378

CLAIMS:

What is claimed is:

1. A method of cleaning a hard surface comprising the steps of activating a peroxygen compound with a complex of formula I:

[M.sub.n (NH.sub.3).sub.6-x (L).sub.x]A.sub.n (I)

wherein M is a transition metal selected from the group consisting of iron, copper, and ruthenium, L is a ligand selected from the group consisting of water, hydroxide, chlorate, perchlorate, (NO.sub.2).sup.-, carbonate, nitrate, halide, and thiocyanate, x is a number of 0 to 5, A is a salt-forming anion, n is a number such that the complex of formula (I) has no charge, and contacting a hard surface with an effective amount of an aqueous cleaning solution comprising the activated peroxygen compound.

2. A method according to claim 1, wherein the peroxygen compound is inorganic.

3. A method of cleaning a hard surface comprising the steps of activating a peroxygen compound with a bridged binuclear complex of a transition metal selected from the group consisting of cobalt, iron, copper, and ruthenium, said complex containing at least 1 ammonia ligand per transition metal atom, and contacting a hard surface with an effective amount of an aqueous cleaning solution comprising the activated peroxygen compound, wherein the complex has a bridge ligand selected from the group consisting of oxo, hydroxo, peroxo, amido, imido, and imino.

4. A method according to claim 3, wherein the complex has at least 4 ammonia ligands per transition metal atom.

5. A method according to claim 1, wherein the transition metal is iron.

6. A method according to claim 3, wherein the transition metal is cobalt.

7. A method according to claim 1, wherein the transition metal has an oxidation

number of +3.

8. A method according to claim 3, wherein the transition metal has an oxidation number of +3.

9. A method according to claim 1, wherein L is a halide or an (NO.sub.2).sup.- group.

10. A method according to claim 1, wherein A is selected from the group consisting of nitrate, hydroxide, hexafluorophosphate, sulfate, chlorate, perchlorate, halide, and an anion of a carboxylic acid.

11. A method according to claim 10, wherein the anion of a carboxylic acid is selected from the group consisting of formate, acetate, benzoate, and citrate.

12. A method according to claim 1, wherein the peroxygen compound is selected from the group consisting of organic per acids, hydrogen peroxide, perborate, percarbonate, and mixtures thereof.

13. A dishwashing detergent composition comprising 0.0025% to 0.25% by weight of a bleach catalyst comprising a complex of a transition metal selected from the group consisting of iron, copper, and ruthenium, said complex containing at least 1 ammonia ligand, 50% to 60% by weight of sodium phosphate, 15% to 25% by weight of sodium carbonate or a mixture thereof with polymeric polycarboxylate, 5% to 15% by weight of sodium perborate or percarbonate, 0.5% to 5% by weight of a bleach activator that eliminates peroxocarboxylic acid under perhydrolysis conditions, 0.5% to 7.5% by weight of a surfactant, 2% to 10% by weight of sodium silicate, and 0.1% to 0.75% by weight of a silver corrosion inhibitor.

14. A dishwashing detergent according to claim 13 comprising 0.01% to 0.1% by weight of the bleach catalyst.

15. A dishwashing detergent according to claim 13 wherein the complex contains at least 5 ammonia ligands.

16. A detergent according to claim 13, wherein the silver corrosion inhibitor is benzotriazole.

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Brief Summary Text (2):
Inorganic peroxygen compounds, more particularly hydrogen peroxide, and solid peroxygen compounds which dissolve in water with elimination of hydrogen peroxide, such as sodium perborate and sodium carbonate perhydrate, have long been used as oxidizing agents for disinfecting and bleaching purposes. In dilute solutions, the oxidizing effect of these substances depends to a large extent on the temperature. For example, with H.sub.2 O.sub.2 or perborate in alkaline bleaching liquors, sufficiently rapid bleaching of soiled textiles is only achieved at temperatures above about 80.degree. C. At lower temperatures, the oxidizing effect of the inorganic peroxygen compounds can be improved by addition of so-called bleach activators for which numerous proposals, above all from the classes of N- or O-acyl compounds, for example polyacylated alkylenediamines, more particularly tetraacetyl ethylenediamine, acylated glycolurils, more particularly tetraacetyl glycoluril, N-acylated hydantoins, hydrazides, triazoles, hydrotriazines, urazoles, diketopiperazines, sulfuryl amides and cyanurates, also carboxylic anhydrides, more particularly phthalic anhydride, carboxylic acid esters, more particularly sodium nonanoyloxybenzenesulfonate, sodium isononanoyloxy-benzenesulfonate and acylated sugar derivatives, such as pentaacetyl glucose, can be found in the literature. By adding these substances, the bleaching effect of aqueous peroxide liquors can be increased to such an extent that substantially the same effects are obtained at temperatures of only 60.degree. C. as are obtained with the peroxide liquor alone at 95.degree. C.

Brief Summary Text (26):
In principle, suitable water-soluble builder components, particularly in detergents of low alkalinity, are any of the builders typically used in machine dishwashing, for example alkali metal phosphates which may be present in the form of their alkaline, neutral or acidic sodium or potassium salts. Examples include trisodium phosphate, tetrasodium diphosphate, disodium dihydrogen phosphate, pentasodium triphosphate, so-called sodium hexametaphosphate, oligomeric trisodium phosphate with degrees of oligomerization of 5 to 1,000 and, more particularly, 5 to 50 and the corresponding potassium salts or mixtures of sodium and potassium salts. They may be used in quantities of up to about 55% by weight, based on the detergent as a whole. Other possible builder components are, for example, organic polymers of native or synthetic origin, above all polycarboxylates, which act as co-builders, particularly in hard-water areas. Suitable builder components of this type are, for example, polyacrylic acids and copolymers of maleic anhydride and acrylic acid and the sodium salts of these polymer acids. Commercially available products are, for example, Sokalan.RTM. CP5 and PA 30 (BASF). Polymers of native origin suitable as co-builders include, for example, oxidized starch, as known for example from International patent application WO 94/05762, and polyamino acids, such as polyglutamic acid or polyaspartic acid. Other possible builder components are naturally occurring hydroxycarboxylic acids, for example mono- and dihydroxysuccinic acid, .alpha.-hydroxypropionic acid and gluconic acid. Preferred builder components include the salts of citric acid, particularly sodium citrate. The sodium citrate used may be anhydrous trisodium citrate and--preferably--trisodium citrate dihydrate. The trisodium citrate dihydrate may be used in the form of a fine- or coarse-particle powder. The acids corresponding to the co-builder salts mentioned may also be present, depending on the pH value ultimately established in the formulations according to the invention.

Brief Summary Text (27):
Besides hydrogen peroxide, suitable oxygen-based bleaching agents are, above all, alkali metal perborate monohydrate and tetrahydrate and/or alkali metal percarbonate, sodium being the preferred alkali metal. Hydrogen peroxide can also be produced by an enzymatic system, i.e. by the use of a combination of an oxidase and its substrate. The use of sodium percarbonate has advantages, particularly in dishwashing detergents, because it has a particularly favorable effect on the corrosion behavior of glasses. Accordingly, the oxygen-based bleaching agent is preferably an alkali metal percarbonate, more particularly sodium percarbonate. Known peroxycarboxylic acids, for example dodecane diperacid, or phthalimidopercarboxylic acids, which may optionally be substituted at the aromatic group, may also be present in addition to or, more particularly, as an alternative to the above-mentioned bleaching agents. Moreover, the addition of small quantities of known bleach stabilizers, for example phosphonates, borates or metaborates and metasilicates and magnesium salts, such as magnesium sulfate, can also be useful.

Brief Summary Text (28):
Standard transition metal complexes known as bleach activators and/or conventional bleach activators, i.e. compounds which form optionally substituted perbenzoic acid and/or peroxocarboxylic acids containing 1 to 10 and more particularly 2 to 4 carbon atoms under perhydrolysis conditions, may be used in addition to the bleach-catalyzing oligoammine complexes described above. Suitable conventional bleach activators are the typical bleach activators mentioned at the beginning which contain O- and/or N-acyl groups with the number of carbon atoms mentioned and/or optionally substituted benzoyl groups. Preferred conventional bleach activators are polyacylated alkylenediamines, more particularly tetraacetyl ethylenediamine (TAED), acylated glycolurils, more particularly tetraacetyl glycoluril (TAGU), acylated triazine derivatives, more particularly 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated phenyl sulfonates, more particularly nonanoyl or isononanoyloxybenzenesulfonate, acylated polyhydric alcohols, more particularly triacetin, ethylene glycol diacetate and 2,5-diacetoxy-2,5-dihydrofuran, and acetylated sorbitol and mannitol, acylated sugar derivatives, more particularly pentaacetyl glucose (PAG), pentaacetyl fructose, tetaacetyl xylose and octaacetyl lactose and acetylated, optionally N-alkylated glucamine and gluconolactone. The combinations of conventional bleach activators known from German patent application DE 44 43 177 may also be used. In one preferred embodiment of formulations according to the invention, 0.5% by weight to 5% by weight of compounds which eliminate peroxocarboxylic acids under perhydrolysis conditions are present in addition to the complex compounds.

Brief Summary Text (37):
In one preferred embodiment, machine dishwashing detergents according to the invention contain 50% by weight to 60% by weight of sodium phosphate, 15% by weight to 25% by weight of sodium carbonate or a mixture thereof with polymeric polycarboxylate, 5% by weight to 15% by weight of sodium perborate or percarbonate, 0.5% by weight to 5% by weight of bleach activator eliminating peroxocarboxylic acid under perhydrolysis conditions, 0.5% by weight to 7.5% by weight of surfactant, 2% by weight to 10% by weight of sodium silicate and 0.1% by weight to 0.75% by weight of silver corrosion inhibitor, more particularly benzotriazole.

Detailed Description Text (2):
A machine dishwashing detergent (C1) containing 45 parts by weight of sodium citrate, 5 parts by weight of sodium carbonate, 31 parts by weight of sodium hydrogen carbonate, 1 part by weight of protease granules and 1 part by weight of amylase granules, 2 parts by weight of nonionic surfactant and also 12 parts by weight of sodium percarbonate and 2 parts by weight of N,N,N',N'-tetraacetylethylenediamine (TAED), a detergent (C2) containing 10 parts by weight of sodium percarbonate and 4 parts by weight of TAED for otherwise the same composition as V1, a detergent according to the invention (M1) containing 0.025 part by weight of nitropentammine cobalt(III) chloride for otherwise the same composition as V1 and detergents according to the invention containing 0.017 part by weight of tetrammine carbonato-cobalt(III) hydrogen carbonate monohydrate (M2), 0.016 part by weight of tetrammine carbonato-cobalt(III) nitrate hemihydrate (M3), 0.022 part by weight of tetrammine carbonato-cobalt(III) chloride (M4) or 0.034 part by weight of

pentammine nitrato-cobalt(III) perchlorate (M5) for otherwise the same composition as V2 were tested as described in the following:

Detailed Description Text (4):
It can be seen that a far better bleaching effect can be obtained by the use according to the invention (M1 to M5) than by the conventional bleach activator TAED alone (C1 or C2). Substantially the same or even slightly better results were obtained when the sodium percarbonate in the detergents according to the invention was replaced by sodium perborate.

CLAIMS:

12. A method according to claim 1, wherein the peroxygen compound is selected from the group consisting of organic per acids, hydrogen peroxide, perborate, percarbonate, and mixtures thereof.

13. A dishwashing detergent composition comprising 0.0025% to 0.25% by weight of a bleach catalyst comprising a complex of a transition metal selected from the group consisting of iron, copper, and ruthenium, said complex containing at least 1 ammonia ligand, 50% to 60% by weight of sodium phosphate, 15% to 25% by weight of sodium carbonate or a mixture thereof with polymeric polycarboxylate, 5% to 15% by weight of sodium perborate or percarbonate, 0.5% to 5% by weight of a bleach activator that eliminates peroxocarboxylic acid under perhydrolysis conditions, 0.5% to 7.5% by weight of a surfactant, 2% to 10% by weight of sodium silicate, and 0.1% to 0.75% by weight of a silver corrosion inhibitor.